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(54) Title: GLAZES (57) Abstract Glazes are applied e.g. to pottery ware or ceramic tiles by a sol-gel process. The sol contains glaze forming precursors. Once the sol has formed a gel on the surface of the ware or tile, the ware may be heated to densify the gel and convert it (at low temperatures) to a vitreous glaze. No intermediate drying step is needed. The final glaze is of increased durability.		

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GLAZES

This invention relates to the application of vitreous glazes to pottery ware and ceramic tiles.

5 It is well known to provide pottery ware and ceramic tiles with a vitreous glaze coating. A typical glaze for example will comprise lead bisilicate. Conventional glazes are prepared by forming a homogeneous melt of glassy material, cooling and grinding to a powder. The
10 powder may then for example be suspended in water, and the resulting suspension is applied to the pottery ware and ceramic tiles to be glazed, e.g. by spraying or dip coating. The items are then dried and passed to a furnace where they are heated to a sufficiently high temperature
15 to refuse the glassy material onto the ware or tile to a vitreous glaze. Typical glazing temperatures are of the order of 1100 to 1200°C.

The application of a glaze at such high temperatures is
20 particularly difficult where the pottery ware or ceramic tile is decorated with colour and/or precious metal transfers. There is a tendency for the glaze to interfere with the decoration. Indeed for in particular fine bone china or porcelain, and for the application of intricate
25 patterns, it is generally the case that the decoration is applied as an overglaze, rather than underglaze,

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decoration. Underglaze decorations are used. However they will generally be used only with low temperature glazes such that they can withstand the glazing temperature without deterioration and/or with a range of 5 colours restricted to those which can withstand highest temperatures.

Pottery ware, in use, has to withstand much harsh treatment. Moreover, in dishwashing machines, which are 10 increasing in popularity, pottery ware is subjected to harsh conditions. Conditions in dishwashing machines are particularly aggressive with regard to alkalinity, temperature and velocity of water/detergent mix. Frequent washing in dishwashing machines has a tendency to 15 eventually lead to fading of colours and removal of metal transfer material. Not only is there a loss of appearance but also there is an environmental problem because some of the conventional transfer materials and pigments contain for example lead and, e.g., cadmium-containing materials 20 which are used in reds and oranges. These materials can be leached from the transfer materials into the dishwasher water and then discharged to the water system. Additionally, under these conditions, there can be a loss of lead from the glaze itself.

25

While the losses of lead and cadmium-containing compounds from pottery ware in this way may be small, it is a matter which is causing increasing concern. Attempts to provide a protective overglaze in conventional manner to decorated 30 pottery ware have not been entirely successful. The problem is to find a glaze which, on the one hand, is soft enough to fuse over transfers at low enough temperature not to interfere with the decoration but, on the other hand, is durable in a dishwasher environment. Softer, 35 lower melting glazes generally tend to be less durable.

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According to the present invention there is provided a method of forming a vitreous glaze on pottery ware or ceramic tiles, which method comprises applying to the ware or tile a coating of a sol comprising one or more organometallic precursors of a vitreous glaze which sols, under the conditions employed, are capable of reacting to form a vitreous glaze, allowing the sol to form a gel on the ware or tile and heating the gel in a single heating step to densify the gel and form a vitreous glaze on the ware or tile.

It has been found that, by the method of the present invention, the heating of the gel form with densification and forming of the vitreous glaze can be carried out in a single heating operation and this requires considerably lower temperatures than are required for the conventional application of vitreous glazes. Peak firing temperatures of 1050 to 1150°C are not uncommon, while using the method of the present invention, a vitreous glaze may be produced even at peak heating temperatures as low as 500°C or even less. Thus using the method of the present invention hard glazes, durable in dishwashing machines, can be applied at appreciably lower temperatures than are conventionally employed and with considerable energy savings. In particular, using the method of the present invention, a durable overglaze may be provided on pottery ware decorated with colour or precious metal transfers without interfering with the decoration. The glaze according to the present invention applied over conventional glaze may also serve to prevent loss of lead from the conventional glaze. A further advantage is that heating to form the glaze may be carried out (and indeed is preferably carried out) immediately after gel formation, which occurs fairly rapidly after dipping.

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Sol-gel technology, which is employed according to the

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present invention, is known per se. The technique has been studied although its mechanism is not yet fully understood. The technique is for example discussed in the Journal of Non-Crystalline Solids, 1988, Volume 100.

5

The sol used according to the present invention may be obtained by dissolving in organic solvent one or more organometallic precursors capable of reacting under the conditions used to form a vitreous glaze. It is important that the glaze is vitreous, rather than crystalline, is hard and has chemical durability. Suitable glazes are based on SiO_2 and at least one of TiO_2 , ZrO_2 and Al_2O_3 .

10

For example:

15

SiO_2 TiO_2 ZrO_2

SiO_2 ZrO_2

SiO_2 TiO_2

SiO_2 Al_2O_3

SiO_2 Al_2O_3 TiO_2

20

SiO_2 Al_2O_3 ZrO_2

SiO_2 Al_2O_3 ZrO_2 TiO_2

mixtures may be suitable.

25

The above glaze systems are obtained, according to the invention, a route involving the reaction of the starting organometallic precursors. While it is not wished to be bound by any theory, it is believed that, in the present of atmospheric moisture, the organometallic precursors hydrolise to form hydroxides which, in their turn, polymerise and cross-link to form the final vitreous glaze coating.

30

In order to ensure homogeneity in the final glaze, it is highly desirable not only that the ingredients of the sol are homogeneous but also that the starting organometallic

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- 5 -

precursors in the sol used have the same or similar reactivity. In order to ensure thus, it may be necessary partially to hydrolise a less reactive organometallic precursor and to hinder a more reactive organometallic precursor.

Suitable sols for use in the present invention comprise an organosilicate compound together with one or more organozirconium, organotitanium or organoaluminium compounds dissolved in an organic solvent. Particularly preferred compositions according to the invention include trialkylorthosilicate together with one or both of a zirconium alkoxide and titanium alkoxide in a lower alcohol. In order to ensure similar reactivity, it may be desirable partially to hydrolise the organosilicate, e.g. by the addition of water and to retard the reactivity of the organotitanium compound using e.g. ethyl acetoacetate.

The proportions of the starting organometallic precursors will be chosen according to the desired properties of the final vitreous glaze coating. It is important the final glaze has chemical durability, is not a polycrystalline ceramic and has an expansion co-efficient close to that of the ceramic body. In general, the final glaze will have a lower limit the composition is likely to crystallise. Likewise the upper limit for ZrO_2 is of the order of 20% by weight of the final glaze. Above this, again crystallisation is likely to occur.

A suitable glaze obtained according to the invention comprises approximately 65% SiO_2 , 20% TiO_2 and 15% ZrO_2 .

The presence of alkaline in the sol composition is to be avoided since its presence will tend to harm chemical durability.

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The sol, on mixing, is generally left to age e.g. for 1 to 4 days. While the mechanism of this ageing process is not fully understood, it is believed that some hydrolysis of the organometallic precursors as a result of reaction with atmospheric moisture leading to some initial polymerisation will occur and also that the homogeneity of the composition increases during ageing.

The sol, generally after ageing, is applied to the pottery ware or ceramic tiles. The application can suitably be by dip coating or by spraying or by ultrasonic or electrostatic application techniques. The form of the sol must of course be suitable for the application method to be employed. For example, for dip coating, the viscosity of the sol will for example be determined by the desired thickness of the coating to be applied.

The organic solvent is then allowed to evaporate off and, e.g. atmospheric water reacts with the organometallic compounds resulting in (further) hydrolysis which, in turn, causes polymerisation and cross-linking to form a gel on the surface of the pottery ware or ceramic tile.

The dried gel is then densified by heating. This should take place as soon as possible after the gel has formed since if it is left too long the gel may dry out and crack and such cracking leads to defects in the final glaze. The heating can be carried out at relatively low temperatures compared to normal glaze firing. In particular it is possible to densify and fuse the gel to form a glaze at a temperature less than half of the melting point of conventional vitreous glazes. The temperature of the densification step will vary according to the ingredients used and the durability of the final glaze. Using the method of the present invention higher durability vitreous glazes can be obtained at

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significantly lower temperatures than using conventional fusing methods. Suitable densification may be carried out according to the invention at below 700°C, preferably 300 to 600°C.

5

Care is required in the densification step to ensure that the original porous structure of the gel is lost to obtain a hard, non-porous vitreous glaze coating.

- 10 Within the term "pottery ware" used herein are included china, porcelain or earthenware and the like.

The vitreous glaze according to the present invention, may be provided over an entire pottery ware article. In this
15 case the vitreous glaze obtained according to the present invention can serve to reduce lead loss from any underlying conventional glaze and to provide a protective glaze for any underlying decoration.

- 20 Alternatively the vitreous glaze according to the present invention may be provided just over, e.g., areas of decoration to provide a protective overlayer. Indeed, and this forms a further feature of the present invention, the sol or gel may be provided as an overlayer on a decoration
25 transfer before application to the pottery ware or ceramic tile.

EXAMPLE

- 30 Preparation of sol (coating solution)

Hydrochloric acid (1ml; 0.01M) mixed with H₂O (1ml) were added to a mixture of tetraethyorthosilicate (25ml) and ethanol (68ml). The resulting mixture was stirred
35 thoroughly.

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Titanium isopropoxide (8.17ml), propan-2-ol (20ml) and ethyl acetoacetate (2.6ml) were mixed in a separate beaker.

- 5 The titanium isopropoxide-containing mixture was added, dropwise over about 40 minutes, to the tetraethylorthosilicate-containing solution; stirring magnetically throughout.
- 10 The resulting mixture was sonicated for 15 minutes. The zirconium propoxide (6.3ml) was added dropwise with stirring.

- 15 The resulting mixture was covered and stored for ageing under refrigeration for four days before use.

Coating

- 20 China plates, with colour transfer decoration, to be glazed were first cleaned. The items were placed in an ultrasonic bath in a solution of 2.5% solution of Decon at 40°C and sonicated for 10 minutes. The items were rinsed with water, methanol and then acetone and dried at 50°C for about 20 minutes.

- 25 The sol coating solution, prepared as above, was placed into a bath and each item to be coated was dipped into the solution at a maximum speed of 19mm/min until fully immersed in the coating solution. the item was then
- 30 withdrawn slowly (5mm/min) such that the solution was allowed to gel on the items.

- The coated plates were then suspended in air and left for at least one hour prior to heating.
- 35

Heating/Densification

The coated items were each heated, in a programmable furnace up to 500°C at a rate of 1°C/minute and the
5 temperature of 500°C was held for one hour.

The dipping, and densification processes were repeated three times. After the third and final densification the items were subjected to an alkaline detergent test, with
10 satisfactory results.

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CLAIMS

1. A method of forming a vitreous glaze on pottery ware and ceramic tiles which comprises applying to
5 the ware or tile a coating of a sol comprising one or more organometallic precursors of a vitreous glaze which, under the conditions employed, are capable of reacting to form a vitreous glaze, allowing the sol to form a gel on the ware or tile,
10 and heating the gel in a single heating step to densify the gel and subsequently form a vitreous glaze on the ware or tile.
2. A method according to claim 1 wherein the sol is
15 obtained by dissolving one or more organometallic precursors capable of reacting under the conditions used to form a vitreous glaze in an organic solvent.
- 20 3. A method according to claim 1 or 2 wherein the glaze is based on SiO_2 and at least one of TiO_2 , ZrO_2 and Al_2O_3 .
4. A method according to any of claims 1 to 3 wherein
25 the sol comprises an organosilicate compound together with one or more organozirconium, organotitanium or organoaluminium compounds dissolved in an organic solvent.
- 30 5. A method according to claim 4 wherein one or more of the organosilicate, organozirconium, organotitanium or organoaluminium compounds is partially hydrolysed or hindered to render the
35 starting organometallic precursors in the sol of the same or similar reactivity.

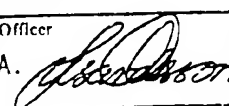
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6. A method according to claim 4 or 5 wherein the sol comprises trialkylorthosilicate and one or both of a zirconium alkoxide and a titanium alkoxide in a lower alcohol.
- 5
7. A method according to any one of claims 1 to 6 wherein the sol component are such as to provide a final vitreous glaze of composition substantially SiO_2 65%, TiO_2 20% and ZrO_2 15% by weight.
- 10
8. A method according to any one of claims 1 to 7 and including the step of ageing the sol for 1 to 4 days after mixing and before application to the ware.
- 15
9. A method according to any one of claims 1 to 8 wherein the heating to densify the gel takes place to a peak temperature within the range of 300 to 700°C.
- 20
10. A method according to claim 9 wherein the peak temperature is in the range of 450 to 550°C.
- 25
11. A method according to any one of claims 1 to 10 wherein the coating is applied to the ware or tile carried as an overlayer or a decoration transfer, such overlayer being in sol or gel from when the transfer is applied to the ware or tile.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 90/01906

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5	C04B41/65	
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C04B	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	CERAMIC ENGINEERING AND SCIENCE PROCEEDINGS. vol. 5, no. 5/6, June 1984, US pages 379 - 383; L. C. Klein: "Oxide coatings from sol-gel process" see page 1, line 1 - page 2, line 3 see page 3, line 3 - page 4, line 46 ---	1-7, 9-10
Y	DE,A,3817240 (CRISTALUX KIRCHBERGER GLAS-GMBH) 23 November 1989 see abstract; claims 1, 3-5, 9, 14 see column 3, line 6 - column 4, line 22 see column 5, lines 18 - 68 ---	1-7, 9-10
A	EP,A,337618 (DOW CORNING CORPORATION) 18 October 1989 see abstract; claim 1, example 1,3 see page 1, line 47 - page 2, line 19 see page 3, line 38 - page 5, line 10 see page 5, lines 31 - 46 ---	1-6, 8-9
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<p>¹⁰ Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	CHEMICAL ABSTRACTS, vol. 90, 1979 Columbus, Ohio, USA T. Takehisa et al: "Tile glazing" page 264; column 1; ref. no. 43093H &JP-A-7899210(Danto Co,Ltd)30.08.1978 see abstract ---	1, 3, 11
A	FR,A,1284245 (MULDER & ZOON N. V.) 02 January 1962 see the whole document ---	1, 3-4, 11
A	US,A,4196004 (M. BERRETZ) 01 April 1980 see column 4, line 36 - column 5, line 16 see column 10, line 51 - column 12, line 50 ---	1, 3, 11

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

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SA 42689

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-3817240	23-11-89	None	
EP-A-337618	18-10-89	US-A- 4842888 JP-A- 1290579	27-06-89 22-11-89
&J---7899210		None	
FR-A-1284245		None	
US-A-4196004	01-04-80	None	

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